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THE COMPRESSIBILITY AND PRESSURE COEFFICIENT OF RESISTANCE OF ZIRCONIUM AND HAFNIUM.

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The data of this paper were obtained in continuation of my program to extend the measurement of compressibility and resistance under pressure to all the pure elements available. I have previously published results[1] for the effect of pressure on the resistance of a very impure specimen of zirconium, made by depositing a covering of zirconium on a core of tungsten. The impurity was so great that the temperature coefficient of resistance was only 0.00004, and the specific resistance was 200×10^{-6}. The pressure coefficient of resistance, in kilogram units, of this impure zirconium, was -4.0×10^{-7}. So far as I know, no previous measurements have been made on the compressibility of zirconium, or on either the compressibility or resistance under pressure of hafnium.

For the material of this investigation I am greatly indebted to Dr. G. Holst, of the Naturkundig Laboratorium, Eindhoven, Netherlands, Philips Gloeilampen Fabrieken. In connection with an investigation of possible commercial uses, both these metals have been prepared in a state of high purity by the Philips Lamp Works.

Two pieces of zirconium were available. The resistance sample was a wire, about 0.050 cm. in diameter and 14 cm. long. The potentiometer method of measurement was used, which demands two current and two potential terminals. It is not possible to solder zirconium by any easy means, and therefore the terminals were attached by spring clips, in a way which has been used for a number of other metals. The compressibility was measured on a piece 2.7 cm. long, about 3 mm. in diameter. It was measured in the same apparatus as that used for many previous measurements,[2] which I have described as "the lever apparatus for short specimens."

Only a single piece of hafnium was available, about 2.6 cm. long and 2 mm. in diameter. The outside surface was not perfectly regular, the appearance being as if the piece were composed of several rather large crystal grains which were slightly staggered with respect to each other. This irregularity of figure is perhaps connected with the fact that the compressibility measurements were much more irregular than usual. Because of the very low resistance of this

specimen (about 0.00112 ohms), the pressure coefficient could be determined only with much less accuracy than usual. I did not attempt to find the variation of pressure coefficient with temperature; neither was it possible to find any departure from linearity between pressure and resistance. It is no more possible to solder hafnium than zirconium, so again connections had to be made with springs. The potential terminals were placed only 1.2 cm. apart, to avoid as far as possible end effects. The current connections at the ends were specially constructed to touch the specimen as nearly as possible at all points around the circumference, so that the lines of current flow inside the specimen should be straight.

In addition to compressibility and pressure coefficient of resistance, the specific resistance, and temperature coefficient of resistance at atmospheric pressure were measured. The temperature coefficient was obtained from measurements at 30° and 75°; the values listed are the average coefficients between 0° and 100° (*i. e.*, $(R_{100} - R_0)/R_0$), obtained by drawing a straight line through the measurements at 30° and 75°.

The results follow. The pressure range was up to 12000 kg./cm.^{2}, as usual.

Zirconium.

Compressibility:

At 30°, $-\Delta V/V_0 = 10.97 \times 10^{-7}p - 7.44 \times 10^{-12}p^2$.

At 75°, $-\Delta V/V_0 = 11.06 \times 10^{-7}p - 7.80 \times 10^{-12}p^2$, pressure in kg./cm.^{2}

At 30°, the average deviation of a single reading from a smooth curve was 0.6% of the maximum pressure effect, and at 75°, 0.7%. The decrease of compressibility with increasing pressure was well marked and far beyond experimental error.

Resistance:

$$\text{At } 30°,\ \Delta R/R\ (0\text{ kg}, 30°) = -4.31 \times 10^{-7}p + 6.5 \times 10^{-12}p^2,$$

$$\text{At } 75°,\ \Delta R/R\ (0\text{ kg}, 75°) = -6.01 \times 10^{-7}p + 5.8 \times 10^{-12}p^2.$$

The resistance decreases under pressure, which is the normal behavior. The coefficient is, however, unusually small, which accounts for the somewhat larger experimental error than usual. At 30° the average deviation of a single reading from a smooth curve was 1.4% of the maximum pressure effect, and at 75°, 1.6%. Expressed in terms of the total resistance, this means that at 30° the

average deviation from a smooth curve was 0.006% of the total resistance, and at 75°, 0.009%. Not much better can be expected, considering the diameter of the specimen, and the fact that the contacts were made with springs.

The specific resistance at 30° was found to be 49.2×10^{-6}, and the mean temperature coefficient between 0° and 100° 0.00403. The latter figure is evidence of the high purity of this material. It is remarkable that the pressure coefficient of the sample originally measured should have been so close to that found above, in spite of the fact that its temperature coefficient and specific resistance showed very high impurity.

Hafnium.

Compressibility:

$$\text{At } 30°, \quad -\Delta V/V_0 = 9.01 \times 10^{-7}p - 2.37 \times 10^{-12}p^2,$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 8.81 \times 10^{-7}p - 2.37 \times 10^{-12}p^2.$$

At 30° the average deviation of a single reading from a smooth curve was 1.7% of the maximum pressure effect, and at 75° 2.0%. The accuracy was not great enough to establish any deviation from linearity in the relative compressibility of hafnium and iron, which is the quantity directly measured. The second degree term in the formulas above comes from the compressibility of iron. It is probable that the second degree term is actually materially larger than given above. Neither is it certain that the compressibility at 75° should be less than that at 30°.

Resistance:

$$\text{At } 30°, \quad \Delta R/R \text{ (0 kg, 30°)} = -10.0 \times 10^{-7}p.$$

The average deviation of a single reading from a smooth curve was 6.0% of the total pressure effect, which means 0.09% in terms of the total resistance. Again I believe that this irregularity is as small as could be reasonably expected in view of the dimensions of the specimen, and the method of connection by spring clips.

The specific resistance at 30° was found to be 35.7×10^{-6}, and the mean temperature coefficient between 0° and 100°, 0.00398. Again the high value of temperature coefficient is presumptive evidence of high purity.

Discussion. The compressibilities listed above are cubic compressibilities, whereas the measured quantities were linear compressibilities. In converting the one into the other, the assumption was

made that the compressibility is equal in all directions. Now this assumption is doubtless not strictly justified, because neither zirconium nor hafnium crystallizes in the cubic system, but instead in the close-packed hexagonal arrangement. However, the assumption of equal compressibility in all directions is probably approximately justified for these two metals, because the axial ratios are such (1.644 for hafnium and 1.593 for zirconium) as to correspond nearly to close packed *spheres*, for which the ratio is 1.63. It must nevertheless be recognized that the assumption of equal compressibility in all directions in a hexagonally close packed arrangement of spheres has not yet been justified by experiment, and should receive such a test.

In general comment on the results we may note in the first place that the compressibilities fit well into the vacant places in the periodic table, as is shown, for example, in Figure 1 of my paper in Proceedings American Academy 62, 207–226, 1927. It is perhaps not to be expected that the compressibility of hafnium should be less than that of zirconium, since in the majority of cases the heavier elements in a given column of the periodic table are more compressible. However, this observation is confined mostly to elements of lower atomic number than hafnium, and it is evident from the figure that there is some reverse tendency at higher atomic numbers.

The pressure effect on resistance has the normal sign in both these elements, but it is rather smaller for each than usual. It is to be noted that the pressure coefficient of resistance of hafnium is greater numerically than that of zirconium, although its compressibility is less. This emphasizes the fact frequently mentioned before that the pressure effect on resistance is not directly concerned with the volume changes produced by pressure.

I am indebted to my assistant, Mr. Stephen Stark, for making the readings of this paper.

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[2] P. W. Bridgman, Proc. Amer. Acad. 58, 175, 1923.